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VOL. 18, SEC. A. OCTOBER, 1940 NUMBER 10

A NEW FORM OF ABRASION TESTER[1]

BY P. LAROSE[2]

Abstract

A machine for testing the abrasive property of textile material is described. This abrasion tester differs from others in the method of renewing the wearing surface. This offers certain advantages.

The following is a description of an abrasion tester which has been in use for some time in the National Research Laboratories, Ottawa, and which has proved to give good results. Its principal advantage over most of the other abrasion testers is that the abrading surface is continually and automatically renewed. This is essential in testing materials that are worn down slowly. As a matter of fact, abrasion tests in which the materials are worn down too rapidly are of little value, since the conditions of wear are too far removed from actual service conditions. Where the same abrading surface, whether emery cloth or some fabric, is used throughout a test, it is evident that, unless the duration of the test is short, the nature of the abrading surface will be changed appreciably during the test. This renders comparison difficult when two materials tested require different times to wear down to the same degree. The tester also allows the use of different materials as the abrading surface; the only necessary qualification is that the material must be available in tape or ribbon form. Two materials have been used in the National Research Laboratories, Ottawa—a fine emery cloth and a heavy cotton webbing.

The fabric to be tested is rubbed back and forth over a cylinder covered with the abrading material. By means of a system of gears, the cylinder is rotated slowly and a second cylinder in contact with the first feeds the abrading tape at the same speed.

Fig. 1 is a photograph of the apparatus showing the most important features. Figs. 2 and 3 are line drawings showing the path followed by the abrading tape and the gear assembly, respectively.

The manner in which the tester functions will be quite clear from these figures. The small circles in Figs. 2 and 3 represent the shafts of all rotating parts and are numbered to correspond.

[1] *Manuscript received August 19, 1940.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 950.

[2] *Chemist.*

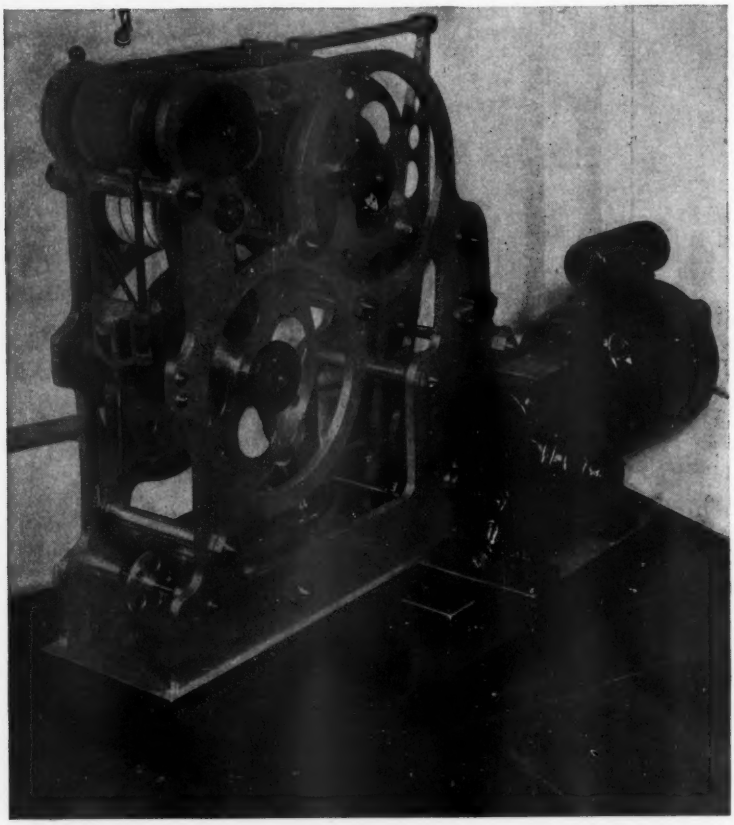

FIG. 1

The abrading material in the form of a long tape $1\frac{3}{4}$ to 2 in. wide is fed from drum (3) on which it is wound. It passes under the idler roller (6) and over the abrading cylinder (1). It then passes over the friction roller (2) on to the receiving drum (5). The tape is fed by the friction between cylinder (1) and cylinder (2) covered with a series of rubber bands. Cylinder (2) is geared to cylinder (1) from which it receives its motion. The abrading tape is kept taut at the feeding end by having a friction brake acting on drum (3) as shown in Fig. 3, and at the receiving end by a friction drive on drum (5) by means of a round spring belt.

Cylinder (1) is driven from a speed reducer motor rotating at 100 r.p.m. coaxial with driving gear (9). The reduction in speed of the abrading cylinder is obtained by means of two worms and gears at (1) and (7) through a shaft fitted with a universal joint. Gear (8) transmits the motion of (9) to (7). The purpose of the universal joint is to permit disengagement of the worm at the

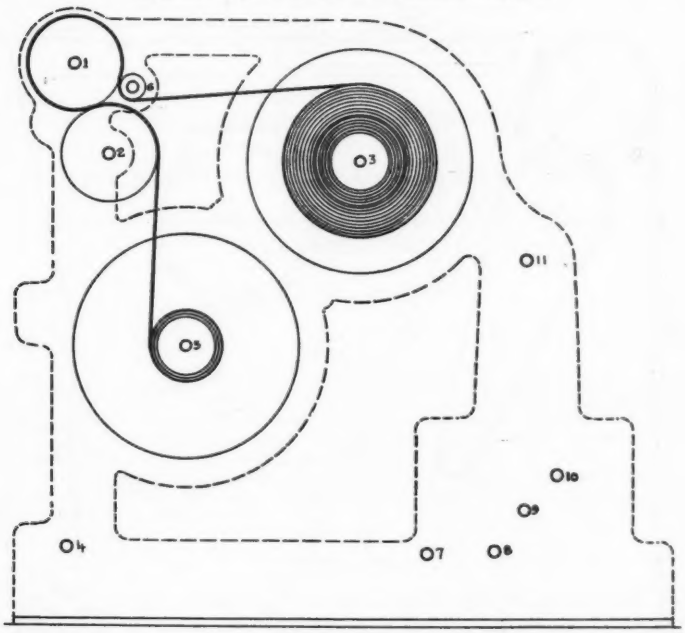

FIG. 2

top of the shaft with gear (1) when the tape is rewound or whenever necessary. This is done by movement of the upper bearing of the shaft to which is fixed a locking lever, not shown in the drawing. The abrading cylinder has a diameter of 3 in. In the present machine, the speed of the cylinder is such that there is a complete renewal of abrading surface in 30 min. This speed has been found to be sufficient for most purposes.

The sample to be tested is cut into a strip $1\frac{3}{4}$ in. wide by about 9 in. between clamps. The upper clamp slides in a horizontal guide and is directly connected to one end of a link, the other end of which is connected to a swinging lever or beam, oscillating around (11). This beam is slotted at the other end to receive a small block fixed eccentrically to a wheel on the driving shaft (9). The dimensions are so fixed that a movement of 3 in. is given to the upper clamp and consequently the sample. The other end of the sample is fixed into a clamp that slides up and down between two guides easily seen on the photograph. The sample is held taut by means of a light spring, attached at one end to the lower clamp and at the other to a gut string, passing around pulley (4), idling on ball-bearings, and tied to the oscillating beam so that it also has a movement back and forth of 3 in., thus maintaining the spring at the same length and consequently a constant tension on the sample. The actual tension exerted on the tester described is of the order of 2 lb. This can be varied, of course, by altering the extension of the spring.

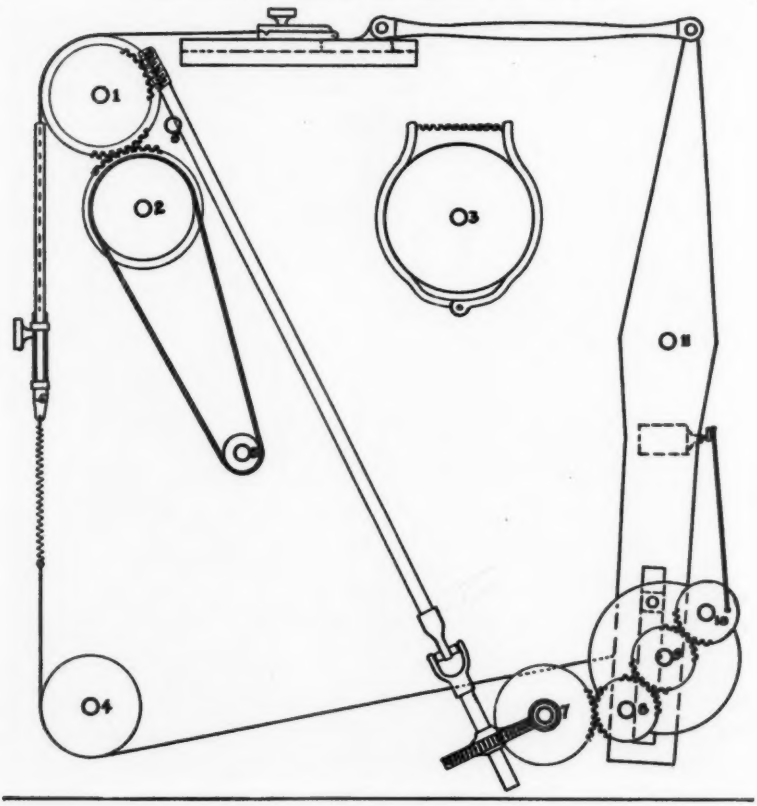

FIG. 3

A revolution counter, to register the number of strokes, functions through an eccentric wheel (10) geared to the main driving shaft.

An automatic stop shuts off the motor when the sample is completely worn out. At that point the lower clamp, pulled down by the tension of the spring, comes against a small pin that trips a mercury switch, thus breaking the circuit.

It is evident that by a simple change of design several samples could be run in parallel with the same driving motor. Each section could be stopped automatically by having the lower clamp strike a lever at the moment of break; this would throw the shaft driving cylinder (1) out of gear, as is done by hand on the present machine.

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THE PROBLEM OF PLASTEIN FORMATION

III. A NOTE ON THE COMPLEXITY OF PEPTIC PLASTEIN IN UREA SOLUTION[1]

BY H. B. COLLIER[2]

Abstract

A solution of plastein in strong urea was injected into guinea-pigs and was found to give a slight anaphylactic reaction. The urea solution was also analysed in the velocity ultracentrifuge, and was shown to contain particles of protein dimensions, but sedimented in a completely inhomogeneous manner. The proteose substrate showed no sedimentation.

It is concluded that, although the plasteins are formed as a result of a true enzymatic synthesis, and have protein properties, they are not definite entities comparable to typical proteins.

Introduction

The problem of the nature of the plasteins has already been discussed in the second paper of this series (1). It was there indicated that although there is some indirect evidence for the view that the plasteins are formed as a result of a true enzymatic synthesis, there has not been any "direct" evidence of an increase in complexity during plastein formation. It was pointed out that Folley's (3) reported failure to demonstrate particles large enough to sediment in the ultracentrifuge was probably due to the circumstance that he employed an alkaline solution of plastein (pH 9.2). Flosdorf, Mudd, and Flosdorf (2) were unable to obtain a clear-cut antigenic effect when plasteins, in suspension or in alkaline solution, were injected into rabbits. However, it is known (4) that denatured proteins may not be antigenic; and the plasteins resemble denatured, rather than native, protein. Therefore there is no definite evidence that the plasteins are *not* protein in nature.

In the experiments to be described, which are of a preliminary nature, advantage was taken of the observation that isoelectric plastein is soluble in concentrated urea solution. This solution was used in testing the antigenicity of the plastein, and was also subjected to an ultracentrifugal analysis.

Experimental

Properties of Peptic Plastein

Peptic plastein was prepared from egg albumin proteose and crystalline pepsin as described in the previous paper. Its isoelectric point was determined

[1] *Manuscript received April 19, 1940.*
Contribution from the Department of Biochemistry, University of Toronto, Toronto, Ont.
[2] *At the time, holder of a personal grant from the Banting Research Foundation. At present, Research Associate, Institute of Parasitology, McGill University, Macdonald College, Que.*

by the method of minimum solubility. A quantity of the plastein was dissolved by the addition of sodium hydroxide, and reprecipitated by varying amounts of hydrochloric acid. After two hours the precipitates were centrifuged off, and the pH and nitrogen content of the supernatant solutions determined. The results as recorded in Table I indicate that the point of minimum solubility is at about pH 5.5.

TABLE I

ISOELECTRIC POINT OF PEPTIC PLASTEIN

pH	Precipitation, % of total N	pH	Precipitation, % of total N	pH	Precipitation, % of total N
9.5	0	6.2	16.6	4.5	15.2
7.3	12.8	5.5	17.6	4.0	12.4
6.7	16.4	5.3	16.7		

Addition of urea (neutral, recrystallized) to a suspension of isoelectric plastein resulted in a clear, not appreciably opalescent, solution. A solution of 6.7 *M* urea at 37° C. was capable of dissolving about 3% of plastein. Dialysis in cellophane against water resulted in recovery of the plastein as a white flocculent precipitate. The plastein in urea resembled untreated plastein in not giving a positive nitroprusside test until after addition of cyanide.

The following tests were carried out on a urea solution of peptic plastein. No active enzyme was present, since the plastein had been dissolved in alkali and reprecipitated.

*Anaphylaxis**

Six guinea-pigs were injected subcutaneously with sensitizing doses of 1 ml. of a solution 6.5 *M* in urea, containing 0.4% plastein and 1% alum. The intoxicating injections were given intravenously after an interval of seven weeks. One normal and four sensitized animals were injected with solutions of 1% plastein in urea. Two sensitized animals were also injected with 1% proteose containing 0.002% crystalline pepsin (the proportion present in synthesis of the plastein). The results of this experiment are summarized in Table II.

The positive symptoms included rapid respiration, sneezing, scratching ears and nose. There was no actual prostration. The controls indicated that the proteose, including pepsin or traces of unchanged albumin, was not responsible for the reaction. Nor did the plastein in urea produce any reaction in an unsensitized animal. The results may be regarded as suggestive, but the experiment should be repeated with a larger number of animals and

**These tests were carried out under the direction of Prof. M. H. Brown and Mr. A. J. Bishop, of the Department of Hygiene and Preventive Medicine, University of Toronto, whose assistance is gratefully acknowledged.*

larger doses of plastein. It is concluded that the plastein in urea may be slightly antigenic, but is not to be compared with a typical native protein.

TABLE II

ANTIGENIC REACTION OF PLASTEIN IN GUINEA PIGS

Animal	Treatment	Reaction
A	Sensitized + 0.5 ml. proteose	Negative
B	Sensitized + 0.5 ml. proteose	Negative
4308	Normal + 0.5 ml. plastein	Negative
3943	Sensitized + 0.5 ml. plastein	Negative
3758	Sensitized + 0.5 ml. plastein	++
3074	Sensitized + 1.0 ml. plastein	Negative
C	Sensitized + 1.0 ml. plastein	++

Ultracentrifugal Analysis

A sample of plastein was submitted to Dr. A. S. McFarlane, of the Lister Institute of Preventive Medicine, London, England, who kindly consented to perform an ultracentrifugal analysis of the material. Isoelectric plastein was treated with 6 *M* urea and dialyzed for five days in cellophane against urea solution. Undissolved plastein was centrifuged off and the clear solution examined in the velocity ultracentrifuge. A sample of the proteose from which the plastein had been prepared was treated in an identical manner. The result of the analysis is reported as follows.

> These two clear solutions behave differently in the ultra-centrifuge. The proteose could not be sedimented at 60,000 r.p.m. in the presence of the 6 *M* urea. Most of the plastein, on the other hand, sediments, but in a completely inhomogeneous manner. Some 10% of the "soluble" N exists as particles which are undoubtedly larger than egg albumin molecules, but so evenly distributed in size that one cannot identify any group which might be regarded as specifically synthesized protein.
>
> . . . . Since inhomogenous aggregation characterizes many denaturation processes it is impossible to deduce in this case—where both alkali and urea have been used—that any real synthesis has taken place.

This analysis demonstrates clearly that the plastein is not a definite entity, as far as particle magnitude is concerned. Nevertheless, since the substrate contained no large particles, and the plastein did, it seems permissible to conclude that these large particles have resulted from the action of pepsin on proteose.

Discussion

The above-mentioned experiments may be regarded as suggestive, rather than conclusive. The urea solution of plastein exhibits a slight degree of antigenicity, and has been shown to contain particles of protein dimensions. Taken in conjunction with the chemical changes reported in the previous paper, it is difficult to avoid the conclusion that plastein formation is a synthetic process, the proteose molecules being combined into larger particles.

Wasteneys and Borsook (5) have suggested that the plasteins have the properties of denatured protein. The ability to form viscous sols and stiff gels indicates that they are probably long chain molecules. But the role of "tyrosine" suggests the presence of linkages other than peptide.

It may be well to emphasize that the use of the term "synthesis" implies here the formation of larger, more complex molecules from proteose. It does not necessarily imply that the resulting plasteins are specifically synthesized typical proteins. They have many protein properties, giving the usual colour tests and being digested by proteinases with liberation of free amino, carboxyl, and reactive "tyrosine" groups. But the results of the experiments here reported indicate that a plastein is *not* a definite homogeneous protein entity. Nor is it to be expected that a typical protein would result from synthesis under conditions so far removed from those in which natural proteins are formed, with enzymes that are probably not responsible for protein synthesis. Whether the phenomenon of plastein formation throws any light on normal protein synthesis is not clear at the present time.

Acknowledgments

The author is indebted to the Banting Research Foundation for a personal grant. He also wishes to acknowledge the continued interest of Prof. Hardolph Wasteneys in this investigation.

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THE REACTION OF POLYSTYRENES WITH BROMINE[1]

By Léo Marion[2]

Abstract

The quantitative determination of the absorption by polystyrenes of oxygen from benzoyl hydrogen peroxide yields low results in all cases. The action of bromine on polystyrenes is a function of the concentration. With relatively higher concentrations of bromine the values obtained for added bromine are often negative. With more dilute solutions the added bromine always has a real value although it is never more than half the theoretical value and often less. In this case also the substituted bromine is low. The results obtained with the more dilute solutions of bromine might be interpreted by the assumption that polystyrenes are mixtures of saturated and unsaturated individuals, if conclusions based on a reaction so thoroughly affected by concentration and yielding in some cases negative values for added bromine were not altogether untrustworthy.

Introduction

The mechanism of polymerization of ethylenic substances has been interpreted in numerous ways although it is now recognized that polymerization processes are chain reactions (3). Whatever the mechanism of formation, the problem of the presence or absence of an unsaturated linkage in the final polymer remains an open question. It is well known that low polymers such as dimers and trimers contain one double-bond, although certain treatment can transform them into fully saturated substances (4). The evidence for the presence of a double bond in polymers of high molecular weight, such as polystyrenes and polyindenes, is based on the absorption of bromine by the polymers and is very conflicting. Brunner (8), working with Staudinger, found that polystyrenes added a fraction only of an atom of bromine per molecule. Whitby and Katz (11, 12, 13), on the other hand, claimed that polyindenes and polystyrenes added approximately two atoms of bromine per molecule as required theoretically by one double bond. A few years later, however, Risi and Gauvin (4) failed to duplicate the results of Whitby and Katz. They could find no evidence of unsaturation in polystyrenes and polyindenes of high molecular weight and concluded that the polymers were fully saturated. At about the same time, Staudinger and Steinhofer (9) confirmed the findings of Brunner and claimed further that the amount of bromine added increased with the time of the reaction and that it amounted to about two atoms after three days.

In the investigation of polystyrenes with Raman spectra Signer and Weiler (6) failed entirely to detect the line 1640 which corresponds to an aliphatic double bond and concluded that polystyrenes, like ethyl benzene, contain no double bond. This may not be conclusive, however, since in molecules as large as those of polystyrenes a single double bond may well be masked.

[1] *Manuscript received May 9, 1940.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 936.

[2] *Chemist.*

The present author was asked by Dr. Whitby to undertake an independent study of the titration of polystyrenes with bromine. From the discordance of results already published by various authors it is fairly obvious that the use of bromine is unsatisfactory. In other instances, such as with fats, it is well known to yield erratic results and to be dependent on concentration. An attempt was therefore made to detect the presence or absence of a double bond in polystyrenes by the action of benzoyl hydrogen peroxide. The results obtained were inconclusive and the reaction of bromine with polystyrenes was reinvestigated.

Experimental

Fractionation of Polystyrenes

Styrene was prepared by Sabetay's method (5) and purified by treatment with anhydrous calcium chloride followed by distillation under diminished pressure over sodium. It was polymerized, according to the usual method, by heating in a sealed tube at 170° C. for 72 hr. For fractionation, the total polymer (133 gm.) was dissolved in benzene (1200 cc.) and methanol added, drop by drop, until the solution became permanently turbid. On standing, it separated into two liquid layers (*A* and *B*), which were separated. Each layer, after similar treatment, again produced two layers, which were separated, the lower layer from *A* being combined with the top layer from *B*. The process was carried out five times, the bottom layer of one fraction being combined with the top layer of the next at each step. The fractions were then precipitated by the addition of an excess of methanol, and dried by rubbing in a mortar under methanol.

Molecular Weights of the Polystyrenes

All molecular weights, except one, were determined cryoscopically in benzene solution. In all cases, the actual figure found is given, although the depression in freezing point obtained was so low and the molecular weights so high that the author has no illusions concerning the accuracy of such determinations. Furthermore, the polystyrene fractions are obviously not homogeneous and the molecular weights obtained are averages. The exception referred to above gave such a low depression in freezing point that the molecular weight was determined viscosimetrically by Staudinger's method.

Oxidation of Polystyrenes

The benzoyl hydrogen peroxide used was prepared in chloroformic solution by the method of Brooks and Brooks (1). In each case, to the cooled solution of polystyrene in chloroform (10 cc.) the chloroformic solution of benzoyl hydrogen peroxide (1 cc.) was added and the solution allowed to stand 45 hr. in the refrigerator. Aqueous potassium iodide was then added and an excess of aqueous sodium bicarbonate to neutralize the liberated benzoic acid. The free iodine was titrated in the presence of starch with 0.0954 *N* sodium arsenite solution. A blank was run with each determination.

The results were worked out as follows:

$$\frac{N \times 8 \times (\text{Vol. of } Na_2As_2O_3) \times \text{mol. wt.}}{1000 \times \text{wt.}} = \text{Oxygen (in gm.) absorbed per mole.}$$

Preparation of Di-indene

Indene (100 gm.) was refluxed for 10 hr. with coarsely ground pumice (10 gm.) and 23% hydrochloric acid (100 cc.). After cooling, the product was collected in ether, washed free of acid, dried, and fractionated *in vacuo*. It yielded unchanged indene and a fraction, b.p. 160–165° C. at 1 mm. (36 gm.), which crystallized on cooling. It was recrystallized from ethyl alcohol, m.p. 55 to 56°.* In order to ascertain that the product in hand was really di-indene, the dibromide was prepared and recrystallized from ether, m.p. 126°. Stobbe and Färber (10) give 120 to 122°. In accordance with the literature, di-indene, when oxidized with potassium permanganate in acetone, gives rise to phthalic acid and α-hydrindone, m.p. 42° (oxime, m.p. 146°; semicarbazone, m.p. 243°).

TABLE I

REACTION OF POLYSTYRENES WITH BENZOYL HYDROGEN PEROXIDE

Sample	Wt., gm.	Mol. wt.	Time of reaction, hr.	Vol. of $Na_2As_2O_3$, cc.			Oxygen involved		Per cent oxygen found to oxygen calc.
				Blank	Solution	Diff.	Found	Calc.	
1	0.2226	1180	45	10.30	10.07	0.23	0.00018	0.0030	6
1	0.1740	1180	45	10.30	10.01	0.29	0.00022	0.0024	9
2	0.1650	4435	45	10.30	10.07	0.13	0.0001	0.0006	16.7
2	0.1958	4435	45	10.30	9.98	0.32	0.00024	0.0007	34.3
3	0.1981	3380	45	10.30	9.83	0.47	0.00035	0.0009	38.9
3	0.1846	3380	45	10.30	9.82	0.48	0.00037	0.0009	41.1
4	0.1516	1420	45	10.30	10.15	0.15	0.0001	0.0017	6
4	0.1711	1420	45	10.30	10.14	0.16	0.00012	0.0019	6.3
5	0.1493	2384	45	10.30	10.09	0.21	0.00016	0.0010	16
5	0.2051	2384	45	10.30	10.03	0.27	0.00021	0.0014	15.2
6	0.1452	2210	45	10.30	9.97	0.33	0.00025	0.0010	18.1
6	0.2153	2210	45	10.30	9.99	0.31	0.00024	0.0016	16.1
Styrene	0.1388	104	40	21.96	2.28	19.68	0.0150	0.0213	70.4

Bromination of Polystyrenes and Di-indene

The procedure adopted was that of McIlhiney (2), according to which it is possible to differentiate between added and substituted bromine. In all cases the sample was dissolved in purified chloroform (10 cc.) and a chloroformic solution of bromine added (the normality and volume used are given with the tabulated results). The solution was allowed to stand at room temperature in the dark for a time specified with the results. A 10% solution of potassium iodide (25 cc.) was then added and the liberated iodine titrated against a starch indicator with sodium thiosulphate of a normality approximately

* *All melting points are corrected.*

equal to that of the bromine solution used. A 2% solution of potassium iodate (2 cc.) was then added to oxidize the free hydrobromic acid and the solution again titrated with sodium thiosulphate. The results were calculated as follows:

$$\frac{N \times 79.92 \times \text{cc. of } Na_2S_2O_3 \times \text{mol wt.}}{1000 \times \text{sample}} = \text{Bromine (in gm.) added per mole.}$$

$$\text{cc. of } Na_2S_2O_3 = (\text{Vol. of } Na_2S_2O_3 \text{ used in first titration}) - 2(\text{vol. of } Na_2S_2O_3 \text{ used after addition of } KIO_3)$$

$$\frac{N \times 79.92 \times (\text{Vol. of } Na_2S_2O_3 \text{ after } KIO_3) \times \text{mol. wt.}}{1000 \times \text{sample}} = \text{Bromine (in gm.) substituted per mole.}$$

The results of the bromination experiments are tabulated in Tables II to VII.

Results

The oxidation of various polystyrene fractions with benzoyl hydrogen peroxide (Table I) gave fairly consistent checks, but the highest quantity of oxygen absorbed was only about 40% of the theoretical and in most cases it was much lower. It is apparent that such results do not justify any conclusion concerning the presence or absence of a double bond in polystyrenes. It must be remembered, however, that the results are no more accurate than the molecular weights that are involved in the calculations.

In order to study the effect of time and concentration on the course of the reaction of bromine with the polymers, a preliminary investigation was made with the crystalline dimer, di-indene. In Table II are given the results of the titration of di-indene with $N/10$ bromine after gradually increasing times of reaction. With this concentration the added bromine is close to the theoretical value up to eight hours but afterwards goes down rapidly, although there is always some substitution even with the shortest time of reaction. With $N/30$ bromine, on the other hand, the addition approaches the theoretical value even after 24 hr. and substitution is almost always nil (Table III).

When a polystyrene of average molecular weight 8450 is treated similarly, there is always some substitution with $N/10$ bromine and the amount of added bromine is very erratic, the value being sometimes negative (Table IV). With $N/30$ bromine, however, the values obtained for added bromine are always real and vary between 0.6 to 1 atom. They seem to be constant between 5 and 24 hr. Hence, the highest value obtained is only half the theoretical. With this concentration the substituted bromine is kept low.

A series of 11 polystyrenes of average molecular weight varying from about 1200 to 4400 was then titrated in duplicate with both $N/10$ and $N/30$ bromine with a reaction time of 22 to 24 hr. (Tables VI, VII). With $N/10$ bromine

TABLE II

REACTION OF DI-INDENE WITH *N*/10 BROMINE IN CHLOROFORM

Sample	Wt., gm.	Temp., °C.	Time, hr.	Vol. of $Na_2S_2O_3$, cc.		Bromine added per mole		Bromine substituted per mole		Mol. wt.
				1st titration	2nd titration	Gm.	Atoms	Gm.	Atoms	
66	0.1065	23	0.5	9.93	0.56	155.2	1.94	9.86	0.12	232
67	0.1038	23	1	9.83	0.74	151.0	1.89	13.38	0.17	232
68	0.1110	23	2	10.22	0.61	152.1	1.90	10.30	0.13	232
81	0.1211	24.6	8	11.21	0.73	148.7	1.86	11.14	0.14	232
82	0.1000	24.4	18	8.60	0.22	132.2	1.66	4.06	0.05	232
27	0.0716	22.5	22	15.64	6.07	93.35	1.17	161.9	2.02	232
65	0.1089	22	24	23.57	9.02	93.53	1.17	155.3	1.94	232

NOTE:—*In each case, 30.0 cc. of N/10 bromine solution was used. In Experiments 66, 67, 68, 65, the normality of the sodium thiosulphate was 0.1012; in Experiments 81 and 82, it was 0.0996 and in Experiment 27 it was 0.1030.*

TABLE III

REACTION OF DI-INDENE WITH *N*/30 BROMINE IN CHLOROFORM

Sample	Wt., gm.	Temp., °C.	Time, hr.	Vol. of $Na_2S_2O_3$, cc.		Bromine added per mole		Bromine substituted per mole		Mol. wt.
				1st titration	2nd titration	Gm.	Atoms	Gm.	Atoms	
90	0.1043	22	1	23.87	0.05	158.4	1.98	0.33	0.004	232
94	0.0966	20.5	5	22.01	0.01	158.4	1.98	—	—	232
91	0.0998	20	10	22.70	0.40	152.5	1.91	2.79	0.35	232
92	0.1005	22	18	23.12	0.05	159.2	1.99	0.34	0.004	232
93	0.0934	22	24	21.18	—	157.7	1.97	—	—	232

NOTE:—*In each case 40.0 cc. of N/30 bromine solution was used, and the normality of the sodium thiosulphate was 0.0375.*

TABLE IV

REACTION OF POLYSTYRENE WITH *N*/10 BROMINE IN CHLOROFORM

Sample	Wt., gm.	Temp., °C.	Time, hr.	Vol. of $Na_2S_2O_3$, cc.		Bromine added per mole		Bromine substituted per mole		Mol. wt.
				1st titration	2nd titration	Gm.	Atoms	Gm.	Atoms	
73	0.3129	22.6	1	0.32	0.11	21.84	0.27	24.03	0.30	8450
75	0.3215	23.5	2	0.42	0.16	21.26	0.27	34.01	0.43	8450
74	0.3751	23.6	5	0.51	0.17	30.48	0.38	30.48	0.38	8450
76	0.3021	24.2	8	0.39	0.22	− 11.14	−0.14	48.98	0.61	8450
26	0.5121	22.5	22	5.48	3.80	−287.8	−3.6	516.0	6.46	8450
79	0.3137	25	48	0.54	0.12	64.33	0.8	25.73	0.32	8450
80	0.3214	24	72	0.53	0.11	64.88	0.81	23.02	0.29	8450

NOTE:—*In each case 20.0 cc. of N/10 bromine solution was used. In Experiments 73, 75, the normality of the sodium thiosulphate was 0.1012; in Experiments 74, 76, 79, 80 it was 0.0996 and in Experiment 26 it was 0.1030.*

TABLE V

REACTION OF POLYSTYRENE WITH *N/30* BROMINE IN CHLOROFORM

Sample	Wt., gm.	Temp., °C.	Time, hr.	Vol. of $Na_2S_2O_3$, cc.		Bromine added per mole		Bromine substituted per mole		Mol. wt.
				1st titration	2nd titration	Gm.	Atoms	Gm.	Atoms	
83	0.3009	22	1	0.77	—	66.49	0.83	—	—	8450
84	0.3020	20.5	2	0.71	0.06	49.48	0.62	5.08	0.006	8450
85	0.3133	20.5	5	1.04	—	84.07	1.05	—	—	8450
86	0.3021	20	10	1.06	0.06	78.80	0.98	5.03	0.006	8450
87	0.3094	22	24	1.39	0.21	79.40	0.99	17.19	0.22	8450
88	0.3110	22	48	1.49	0.40	56.19	0.70	32.57	0.41	8450
89	0.3072	20.5	72	1.50	0.45	49.46	0.62	37.10	0.46	8450

NOTE:—*In each case 20.0 cc. of N/30 bromine solution was used, and the normality of the sodium thiosulphate was 0.0375.*

TABLE VI

REACTION OF POLYSTYRENES WITH *N/10* BROMINE IN CHLOROFORM

Sample	Wt., gm.	Temp., °C.	Time, hr.	Vol. of $Na_2S_2O_3$, cc.		Bromine added per mole		Bromine substituted per mole		Mol. wt.
				1st titration	2nd titration	Gm.	Atoms	Gm.	Atoms	
33	0.4091	23.8	24	1.22	0.69	− 14.03	−0.18	60.5	0.78	4435
43	0.3101	20.5	24	1.92	1.38	− 97.17	−1.22	159.6	1.99	4435
55	0.4385	22	24	5.47	3.45	− 89.15	−1.12	215.0	2.69	3380
41	0.3320	20.5	24	4.00	2.64	−105.4	−1.32	217.3	2.72	3380
25	0.5324	22.5	22	4.56	2.86	− 27.21	−0.34	98.04	1.23	1517
28	0.4967	23.6	23	9.36	6.47	− 90.01	−1.13	199.5	2.50	1517
30	0.3301	23.6	23	7.36	4.90	−162.1	−2.03	423.2	5.30	2664
31	0.3952	23.6	23	4.84	2.79	− 41.06	−0.51	236.3	2.96	2664
36	0.3740	23.8	24	6.93	3.96	− 46.20	−0.58	216.9	2.71	2158
37	0.3003	23.8	24	4.59	2.31	− 1.74	−0.02	174.3	2.18	2158
49	0.3203	22	24	6.12	4.77	−186.4	−2.33	270.2	3.38	2158
34	0.3000	23.8	24	2.02	1.25	− 15.27	−0.19	39.30	0.49	1180
47	0.3220	20.5	24	1.99	1.40	− 24.01	−0.30	41.48	0.52	1180
35	0.3381	23.8	24	3.48	2.32	− 39.40	−0.49	78.79	0.99	1420
46	0.3220	20.5	24	2.40	1.67	− 33.53	−0.42	59.5	0.74	1420
57	0.2308	23	24	2.30	1.55	−125.0	−1.56	243.5	3.0	4405
58	0.2134	23	24	2.79	1.89	−167.4	−2.09	321.1	4.0	4405
59	0.2823	23	24	1.86	0.76	28.89	0.36	64.57	0.8	2914
60	0.3262	23	24	2.00	0.93	10.29	0.13	68.39	0.8	2914
61	0.2037	23	24	1.78	0.65	38.38	0.48	51.98	0.65	1979
63	0.2516	23	24	1.70	0.61	20.0	0.25	25.42	0.32	1274
64	0.2572	23	24	1.68	0.62	14.58	0.18	20.55	0.26	1274

NOTE:—*In every case 20.0 cc. of N/10 chloroformic solution of bromine was used. The normality of the sodium thiosulphate was 0.1030 in Experiments 25, 28, 30, 31; in the remaining experiments it was 0.1012.*

TABLE VII

REACTION OF POLYSTYRENES WITH $N/30$ BROMINE IN CHLOROFORM

Sample	Wt., gm.	Temp., °C.	Time, hr.	Vol. of $Na_2S_2O_3$, cc.		Bromine added per mole		Bromine substituted per mole		Mol. wt.
				1st titration	2nd titration	Gm.	Atoms	Gm.	Atoms	
152	0.3028	24	24	0.56	—	24.58	0.31	—	—	4435
167	0.3094	22.7	24	0.70	—	30.06	0.38	—	—	4435
153	0.3009	22.7	24	1.79	0.56	22.55	0.28	18.85	0.24	3380
154	0.3296	22.7	24	2.06	0.57	28.27	0.35	17.52	0.22	3380
149	0.3006	24	24	1.69	0.47	11.34	0.14	7.11	0.09	1517
150	0.3101	24	24	1.71	0.45	11.88	0.15	6.60	0.08	1517
147	0.3136	24	24	2.41	0.56	32.85	0.41	14.26	0.18	2664
148	0.3114	24	24	2.33	0.55	31.53	0.40	14.10	0.18	2664
145	0.3100	24	24	3.47	0.82	38.17	0.48	17.10	0.21	2158
146	0.3148	24	24	3.50	0.88	35.74	0.45	18.07	0.23	2158
155	0.3388	22.7	24	0.84	0.22	4.17	0.05	2.30	0.03	1180
156	0.3144	22.7	24	0.80	0.26	3.15	0.04	2.92	0.04	1180
157	0.3056	22.7	24	0.80	0.38	0.56	0.007	5.29	0.07	1420
158	0.3008	22.7	24	0.71	0.35	—	—	4.84	0.06	1420
160	0.0920	23	24	0.65	0.24	24.39	0.30	34.43	0.43	4405
161	0.2660	23	24	2.46	0.77	45.65	0.57	38.21	0.48	4405
162	0.2559	23	24	2.25	0.11	69.28	0.87	3.75	0.05	2914
163	0.2754	23	24	2.57	—	81.49	1.02	—	—	2914
164	0.2275	23	24	3.77	0.27	84.20	1.05	7.04	0.09	1979
165	0.2558	23	24	3.28	0.35	38.50	0.48	5.22	0.06	1274
166	0.2640	23	24	3.32	—	48.00	0.60	—	—	1274

NOTE:—*In each case 20.0 cc. of $N/30$ chloroformic solution of bromine was used, and the normality of the sodium thiosulphate was 0.0334.*

much substitution took place and the values obtained for added bromine were in the majority negative. With $N/30$ bromine all the values obtained for added bromine were low but positive. In two cases (mol. wt., 1180 and 1420) they were nil or almost, and in two cases the added bromine amounted to one atom per molecule. With the $N/10$ solution, no checks could be obtained and the results were completely erratic, whereas with the $N/30$ solution the results for added bromine are tolerably well reproducible and the numbers are always real (positive). Furthermore in the latter instance the substitution is relatively low, whereas in Table VI the substitution is always appreciable and in the majority of cases very high. Wherever the added bromine is expressed by a negative value, substitution has always occurred and the higher the value numerically, the higher the substitution. Since the negative values are sometimes as high as two atoms of bromine, they can scarcely be attributed to experimental error, but they are explainable on the basis of the elimination of substituted bromine as hydrogen bromide, leaving a double bond. This must occur after the first titration, before or during the oxidation with potassium iodate. For instance, if

a = bromine added,

b = bromine substituted = c = bromine liberated as hydrobromic acid,

d = substituted bromine lost as hydrobromic acid,

then, the first titration gives:

$$T_1 = a + b + c$$

and the second titration gives:

$$T_2 = c + d$$

In working out the result, the added bromine is given by the equation:

$$T_1 - 2T_2 = a + b + c - 2c - 2d$$
$$= a - 2d.$$

When $a = 0$ or is much smaller than b,

$$T_1 - 2T_2 = -2d.$$

Discussion

From the results given above it is obvious that the reaction of bromine with polystyrenes is greatly influenced by the concentration of the reagent, and any conclusion based on such results is unsatisfactory. Moreover, because of the uncertainty attaching to the molecular weight of high polymers, the figures obtained in the titrations with bromine do not represent absolute values. The main result obtained is that, independently of the molecular weight, the reaction of polystyrenes with the more dilute solutions of bromine ($N/30$) indicates that some bromine is added. The titrations with dilute bromine solutions might be interpreted as indicating that the polymers are mixtures of saturated and unsaturated individuals. Such a conclusion, however, may not be justifiable because of the erratic results to which an increase in the concentration of bromine may lead.

The evidence for the presence of a double-bond in polyindenes advanced by Whitby and Katz (11, 12, 13) cannot be taken into consideration because they did not differentiate between added and substituted bromine. Furthermore, in their study of polyisoeugenol, polyeugenol, polyisosafrole and polysafrole (14), in which they differentiated between added and substituted bromine, the values that they give for added bromine are unacceptable. From the total bromine absorbed they subtracted the bromine liberated as hydrobromic acid only, and did not double that last figure as required in order to take care of the substituted bromine. When that is done the values for added bromine become zero or negative. Risi and Gauvin (4) in their study of the bromine absorption of polyindenes and polystyrenes of high molecular weight used $N/12.5$ and $N/3$ bromine solutions. In all cases they found no addition but relatively high substitution, and in some cases where they report zero addition, they really obtained a negative value. The solutions of bromine used by these authors were too concentrated. The results obtained by the present author are not in agreement with those of Staudinger and Steinhofer (9). In no case was it observed that the added bromine tended towards the theoretical value as these authors claim. In the titrations with $N/30$ bromine solution (Table V) the added bromine was lower after 48 hr.

than after 24 and lower still after 72 hr. The results obtained now are in best agreement with those of Brunner (8) and it is not possible to agree with Staudinger's statement (7) that "with increasing time of reaction the bromine addition increases more and more, and a marked end point of the reaction cannot be noticed". What seems to occur is that the added bromine reaches a maximum with increasing time of reaction and decreases again.

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PLATINIZED GLASS AS A LABORATORY SUBSTITUTE FOR MASSIVE PLATINUM[1]

By C. C. Coffin[2]

Abstract

A method for sealing platinum through Pyrex glass and the use of platinized glass in the construction of various laboratory devices are described.

Introduction

Although the art of platinizing glass has been known for a long time and has often been described it does not seem to have come into as general laboratory use as its simplicity, usefulness, and low cost would lead one to expect. The widespread use of Pyrex glass and the impossibility of sealing massive platinum directly to Pyrex in the manner so satisfactory with soft glass suggest that platinized Pyrex could profitably replace soft glass and platinum in many instances. In view of a recent paper by Wichers and Saylor (3) on "Sealing Platinum to Pyrex Glass" a description of a somewhat similar method used by the writer for the past few years might be of interest. As platinum and Pyrex are a most useful laboratory combination several other tested applications of the method will be briefly described. As indicated above, this method is based on the use of platinized glass. A feature of the process that is especially noteworthy at the present time is the small amount of platinum used and the remarkably low cost of apparatus so constructed.

Experimental

Making and Applying the Solution

The details of making and applying the platinizing solution have been adequately described by Taylor (2) and need only be outlined here. Two volumes of oil of rosemary are added to one volume of powdered dry platinic chloride crystals. The mixture is stirred to homogeneity and allowed to cool. This will require several hours, as a considerable amount of heat is evolved by a reaction between the oil and the platinum. About three volumes of oil of lavender flowers (the synthetic oil of lavender will not work) is then added. After cooling (heat is again evolved), the "paint" is ready for use. It will keep for an indefinite time if stored in a tightly stoppered bottle.

It is important that the platinic chloride be thoroughly dry. Taylor recommends fusing the salt, which is very hygroscopic, and keeping it liquid until the water has been driven off. To do this without partial reduction requires some caution and experience. An occasional drop of concentrated hydrochloric acid added when the crust begins to form over the almost dry melt helps to prevent serious reduction and subsequent contamination of the

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paint with specks of metallic platinum. The writer has found that unfused platinic chloride stored for some time over concentrated sulphuric acid in a desiccator makes an excellent paint.

The object to be platinized is thoroughly cleaned, warmed, and dipped into, or painted with, the platinizing solution. Excess paint is allowed to drain off (a common error is to have too thick a coat) and the object is slowly and uniformly heated in a smoky flame. In a few minutes the paint, which at first may be almost invisible, will become opaque, then shiny jet black and metallic patches will appear and spread rapidly. At this point the work may be heated to redness to burn in the film, which is of course metallic platinum. Any number of coats may be applied. If too much paint has been used and the film blisters, the work may be buffed before putting on the next coat. Direct flaming and incipient fusion of the surface being platinized is necessary for an adherent film. Taylor points out that it is not possible to apply to infusible surfaces such as quartz or diamond a coat that is adherent. When properly applied to a substance such as glass or glazed porcelain the film becomes an integral part of the surface. A wire soldered to platinized glass and torn off will usually take chips of glass with it.

The Design and Construction of Apparatus

In making a platinum connection to the interior of a Pyrex glass apparatus using little power (e.g., relays, conductivity cells, standard cells, discharge tubes, etc.) the following procedure has always been found to be entirely satisfactory. A rod (1 to 2 mm. diam.), such as is used for stopping "pin-holes" in glass-blowing, is drawn out in the flame from Pyrex tubing, and platinized. Three or four coats are sufficient for the devices mentioned above. This platinized rod is used instead of platinum wire and is sealed into position as though it were ordinary Pyrex glass. It is well to use tweezers for shaping the work. When the joint is complete the platinized rod outside the apparatus is sealed off to form a stud to which a wire can be soldered or which can be immersed in mercury for electrical connection.

This method of combining platinum and Pyrex resembles that of Wichers and Saylor (3) in that a platinum tube is used instead of a wire. In the present case however the tube is filled with the glass on which it is built and is so thin-walled that it could not exist as such without this glass support. In fact the walls are so thin that the ratio of tube diameter to wall thickness never approaches the dangerous lower limit found by Wichers and Saylor, and the "collar cracks" that are always present in their seals have never been observed in those made with platinized Pyrex rod.

An idea of the tightness and resistance of these seals may be had from the following example:—

Eight H-shaped Pyrex standard cell "blanks" were made up with electrodes introduced as described above. To test for tightness all were sealed to a manifold evacuated to a recognizable electrical discharge and sealed off individually. After a month the character of the discharge had not changed

in any cell. They were then opened, filled with mercury, and the resistance of the leads was determined. All showed a resistance (both leads) of between 0.5 and 1 ohm. They were then cleaned, filled as Weston standard cells, sealed off, and mounted with their platinized studs in mercury pools. These cells, some of which have had hard usage, are now six years old and all still have their original e.m.f.

Platinized Pyrex has features other than low cost to recommend it for general laboratory use. The fact that a not very experienced glass-blower can, with Pyrex, make devices that are relatively permanent compared to those that would be produced by his efforts if he used soft glass is not without importance. Pyrex is a good resistance glass, is mechanically strong, and, above all, is so thermally stable that apparatus such as electrodes can be flamed without danger of breakage. This ability to withstand flaming as well as the large surface (cf. wire electrodes) presented to the solution are important points in connection with quinhydrone and similar electrodes. For conductivity cells the variety of design possible and the rigidity of the electrodes are important. The simple dipping cell with glass-rigid electrodes is much more practicable than such a cell with massive platinum electrodes, which are apt to bend and change the cell constant with the slightest abuse. Platinized glass can of course be coated with spongy platinum black just as readily and in exactly the same way as massive platinum. Very simple forms of hydrogen, quinhydrone, and oxidation-reduction electrodes are readily made with platinized soft or Pyrex glass. Newberry (1) has commented very favourably on quinhydrone electrodes of metallized glass.

Attempts to improve and economize on the conventional silver coulometer may not be without interest. For certain work the ordinary platinum crucible is too small—in a prolonged experiment the silver crystals are apt to grow from cathode to anode and cause a short circuit. The use of the larger platinum evaporating dishes (25 to 30 gm.) means more expense and smaller accuracy. Excellent coulometer dishes weighing 10 to 12 gm. have been made by platinizing the inside of the bottom half of an ordinary Dumas bulb. Very light-weight bulbs may be obtained and are easily cut by leading a crack with a hot tool. The edge of the resulting dish should be ground down with emery on a glass plate. To prevent change of shape while being flamed it is necessary to support the dish in a close-fitting mould of asbestos cement. A small brass clip on the edge of the dish makes electrical connection when it is being used as a coulometer.

Such a metal-to-glass seal cannot of course be expected to carry much current unless an inconveniently large number of "coats" are applied. However, 10 to 15 applications have been found to be capable of handling several amperes so that light and rigid electrodes for electrolytic analysis may be made in this way. The glass tube may be bent to any desired shape (spirals, stirrers, etc.) after platinizing.

Taylor (2) has discussed the use of platinized glass in the construction of resistances which unfortunately are not very stable. He also points out that

flawless mirrors for optical work require specially prepared paint but are otherwise not difficult to prepare. The writer has found that rough mirrors for radiation shields are readily made with paint prepared as described. Since they are not attacked by mercury these shields are useful in vacuum systems using mercury pumps and McLeod gauges. Other uses will doubtless suggest themselves.

It is hoped that this note will serve to call attention to a useful and inexpensive technique that seems to be overlooked in many laboratories.

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THE VISCOSITY OF CARBON DIOXIDE IN THE CRITICAL REGION[1]

By S. N. Naldrett[2] and O. Maass[3]

Abstract

Measurements of the viscosity of carbon dioxide in the critical region have been made with great precision by means of an oscillating disc viscosimeter. The variation of viscosity with temperature at constant density has been determined for 14 different densities. Isothermals have been evaluated from a plot of the isochores. One isothermal was determined directly and is in agreement with those determined indirectly.

The form of the viscosity-temperature isochores is not the same as that found by Mason and Maass (12) for ethylene, in that there is no minimum at the critical temperature nor even up to 7° C. above. For the region just above the condensation temperature, the viscosity is more dependent on density than on temperature; the isochores are almost flat and are well separated. However, the isothermals are spread between an upper and a lower limit of density, showing that viscosity is not entirely independent of temperature. Time lags were observed in the present investigation in the opposite direction to those observed by Geddes and Maass (9); this would appear to decrease the strength of their claims that the time lags that they observed are due to the formation of a structure in the liquid state.

Introduction

The fundamental purpose of the investigations being carried out in this laboratory is to obtain information regarding the structure of the liquid state. In the critical region, where the transition from the liquid state to the gaseous occurs, any change in the physical properties of a substance caused by differences in structure between liquid and gas should be most pronounced. The phenomenon of viscosity of a gas shows a fundamental difference from the viscosity of a liquid. For example, the viscosity of a gas increases with rise in temperature, whereas that of a liquid decreases. Hence the investigation of viscosity in the critical region should be of considerable interest.

Only a few investigations of this nature are reported in the literature. Phillips (17) studied carbon dioxide using a capillary flow method. He found that the form of the viscosity-pressure isothermals was similar to that of the density-pressure isothermals expressed by van der Waal's equation, except that they crossed one another. The isothermals were found to cross before liquefaction occurred; this indicates that the system behaves as a liquid before condensation occurs. The values of viscosity, η, at all temperatures, if plotted against density, d, were found to lie on one line; this would appear to indicate that η is more dependent on density than on temperature. That is, the change in η due to the small difference in velocity caused by a change in temperature is not as great as the effect due to the great alteration of intramolecular distances in the critical region. Between $d = 0.2$ gm. per cc. and $d = 0.7$, η is a linear function of d^2. This is taken to mean that in this region

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of rapid change of density with temperature or pressure, change in η is due entirely to change in attraction of two layers of fluid, for this would be proportional to d^2. That is, η in this region depends on the $\frac{a}{v^2}$ term of van der Waal's equation. At higher densities, alteration in the kinetic energy of the molecules begins to play a larger part, whereas at lower densities the attraction between molecules becomes quite negligible.

Schröer and Becker (19) made observations of the viscosities of ethyl ether and of carbon dioxide in the critical regions of these substances. A falling ball viscosimeter was used, with a reported accuracy of 0.5 to 1%. They found that the isothermals in the viscosity-pressure diagram of ethyl ether resemble density-pressure isothermals, in qualitative agreement with the observations of Phillips on carbon dioxide. Contrary to the findings of Phillips, however, Schröer and Becker found that the viscosity is independent of temperature only for densities below a certain limit. From a point below $d = 0.1$ gm. per cc. the isothermals in the viscosity-density diagram begin to diverge, and at $d = 0.5$ gm. per cc., the limit of their observations, they are still divergent.

Clark (5, 6, 7) examined ethyl ether by means of an uncalibrated oscillating cylinder, expressing the results as the logarithmic decrements. He found the viscosity of the liquid phase decreased steadily on heating, passed through a minimum in the neighbourhood of the critical temperature, and rose rapidly above that temperature. On cooling, η was lower than on heating until the temperature was about 20° C. below the critical. Hysteresis persisted as high as 70° C. above the critical temperature. For the vapour phase η increased as the temperature was raised and the hysteresis was less. In his later investigation he found that stirring virtually eliminated the discontinuity, and he also considered that impurities had affected the earlier work. However, he still considered the classical theory of continuity according to van der Waal's equation as insufficient, and favoured the liquidon-gason theory enunciated by Traube (21, 22, 23).

The precision was poor in all the work mentioned above. Mason and Maass (12) have reported an investigation in which the precision has been very greatly increased. The same apparatus has been used in this research. For the purpose, a form of Maxwell's oscillating disc, such as had been used before in this laboratory for precise measurements of viscosity at low pressures (20, 24, 25, 26), was adapted for use at high pressures, by decreasing its dimensions to that it could be placed in a metal bomb. The observations were made through a window of Armour-Plate glass. A few preliminary observations by Mason and Maass on the ethylene system indicated that the viscosity plotted against temperature along an isochore passes through a minimum at the "true critical temperature", as it is defined by Maass and co-workers for ethylene (14, 16). Below this temperature the viscosity decreases with rise in temperature, as is typical of a liquid, and above this temperature the viscosity increases with rise in temperature, as is typical of

a gas. Mason and Maass interpret their findings as further evidence that the liquid state does not cease to exist at the temperature at which the meniscus disappears, but persists to the "true critical temperature" (0.4° higher for ethylene), and that a fundamental change in structure accompanies the transition from liquid to gas.

Experimental

The method used was essentially that used by Mason and Maass (12). It has already been described in detail in previous reports (12, 20, 24, 25, 26) and only sufficient will be repeated to make the present investigation clear.

The fundamental equation for measurement of viscosity by the method of the oscillating disc is:

$$\eta = \frac{\lambda - x}{Ct} \qquad (1)$$

where λ = the logarithmic decrement of the free oscillations,
t = the period in seconds,
x = the damping constant of the suspension,
and C = an instrument constant depending only on the geometry of the viscosimeter system.

In the present investigation the two constants were evaluated by examining two gases, air and hydrogen, the viscosities of which have been accurately determined. λ and t were determined experimentally and substituted in Equation (1) with the known values of η for each gas. From the two equations so obtained, the two constants C and x were calculated. The equation could then be used for the calculation of absolute viscosities by measuring λ and t for the gas being examined.

Calibration of the Apparatus

Air was purified by scrubbing it with concentrated sulphuric acid and with 40% aqueous potassium hydroxide; it was then dried over phosphorus pentoxide. Rigden's data (18) for the viscosity of air was used, taking $\eta_{30.20°\,C.} = 1865.8 \times 10^{-7}$ poises. Hydrogen was prepared by the use of zinc and dilute hydrochloric acid in a Kipp generator, and was purified by scrubbing it with sulphuric acid followed by potassium pyrogallate in 40% potassium hydroxide; it was then passed through activated charcoal immersed in liquid air. The data of Sutherland and Maass (20) for the viscosity of hydrogen was used, after it had been corrected by substituting the data of Rigden for the viscosity of air in their calculations, in place of the probably less accurate data available at the time of their investigation. The viscosity of hydrogen was taken to be $\eta_{30.20°\,C.} = 899.3 \times 10^{-7}$ poises. The data for the calculation of the instrument constants are given in Table I. Substituting these data in Equation (1) and solving the two simultaneous equations obtained gives $C = 10.32_0$ and $x = 0.0999 \times 10^{-2}$. Hence Equation (1) becomes:

$$\eta = \frac{\lambda - 0.0999 \times 10^{-2}}{10.32t}. \qquad (2)$$

Method of Filling the Bomb

After the apparatus was calibrated, the bomb was filled with carbon dioxide. The gas was purified by several sublimations, between which the gas was dried over phosphorus pentoxide. The vacuum pump was applied to the solid carbon dioxide while it was immersed in liquid air, to remove any permanent gases, and the first and last fractions of gas evaporating were discarded at each sublimation. Four or five sublimations were carried out with each sample of gas.

The gas was finally measured in a calibrated 50-litre Pyrex flask and condensed into a steel filling bomb equipped with two valves, one of which lead to the glass purification and measurement apparatus, and the other to the viscosimeter bomb. After the carbon dioxide was condensed in the steel filling bomb, the valve leading to the glass apparatus was closed. The valve leading to the bomb containing the viscosimeter was then opened and the carbon dioxide was evaporated. The valve to the viscosimeter bomb was then closed and the gas left in the filling bomb was allowed to expand into the glass apparatus, where it was measured. In this manner the net amount of gas in the viscosimeter bomb was known. From the known volume of the system, the density could be calculated. Similarly, when it was desired to change the density in the bomb, some of the gas was allowed to escape into the glass apparatus, where it was measured. To calculate the amounts of gas involved, the data of Cooper and Maass (8) were used for the deviation from the ideal gas law.

Method of Making Observations

The bomb was immersed in a water bath, the temperature of which was kept constant to within $\pm 0.01°$ C. by means of a toluene-mercury thermoregulator and a relay.

Viscosity was measured by observing the oscillations of a spot of light reflected through the window of the bomb, from a mirror mounted on the suspension of the disc, on to a ground glass scale, which was corrected for error in graduating and for lack of curvature. The logarithmic decrement of these oscillations was calculated according to the method described by Mason

TABLE I

CALIBRATION OF THE APPARATUS

$\lambda \times 10^{-4}$	t, sec.	$\lambda \times 10^{-4}$	t, sec.
With hydrogen; press., 75 cm.; temp., 30.20° C.		*With air; press., 75 cm.; temp., 30.20° C.*	
2.961	30.88	6.034	30.88
2.959	30.88	6.030	30.86
2.951	30.86	6.029	30.86
2.962	30.88	6.030	30.88
2.963	30.90	Av. 6.030$_5$	30.87
Av. 2.959	30.88		

and Maass (12); the period t was determined by averaging the time for 6 to 10 complete oscillations as measured by means of a stopwatch. These quantities were substituted in Equation (2) to calculate η. At least four, and usually more observations were made and averaged for each of the values of η tabulated.

Results

Isochores

The variation of viscosity with temperature at constant density was determined for 14 different densities. The data are presented in Fig. 1. All the data were obtained by cooling the system down after it had been heated for several hours to a temperature five or six degrees above the critical temperature. The reason for this will be discussed later. For purposes of reference, probably the best values for the critical constants of carbon dioxide

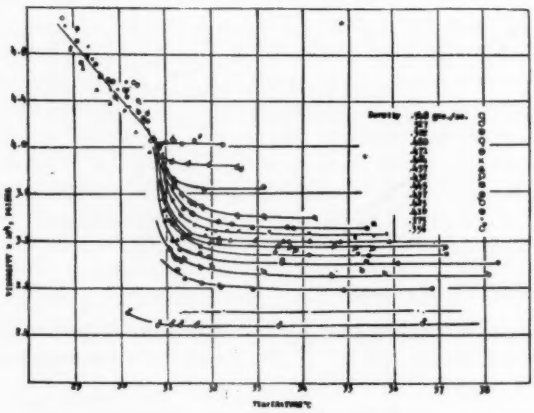

FIG. 1. *Isochores of carbon dioxide.*

are those of Michels, Blaisse, and Michels (15) who find $d_c = 0.467$ gm. per cc. and $t_c = 31.04 \pm 0.01°$ C. from an examination of the $P.V.T.$ relations. None of these isochores were completed by cooling the system down once from above the critical temperature, but all the points had not been obtained until the procedure had been repeated at least twice. Since all the points fall on the same curve nevertheless, it is evident that they are equilibrium values. Moreover, some of the isochores were deliberately repeated with a different sample of carbon dioxide in the bomb. No discrepancies can be observed between the observations made with different fillings of the bomb. This demonstrates that the purity of the carbon dioxide and the means of measuring it are reliable.

It will be observed that the isochores are well differentiated above the critical temperature, but that they converge at the point of condensation. After condensation had begun, the accuracy of the observations was much less and was not sufficient to show the variation of η with density for the liquid,

which is apparently much less than that for the system above the critical temperature.

None of these isochores show a minimum such as that found by Mason and Maass (12) for ethylene, although observations were made up to 7° C. above the critical temperature.

Isothermals

Isothermals showing the variation of viscosity with density at constant temperature have been evaluated from a large plot of the isochores shown in Fig. 1. The data obtained and used in drawing the curves shown in Fig. 2 are given in Table II. One isothermal was determined directly at 31.14° C. and is shown in the figure. It is seen to be of the same shape as the isothermals determined indirectly. Further mention of the isothermals will be made later.

TABLE II

ISOTHERMALS

Density, gm. per cc.	Temperature 32.0° C. $\eta \times 10^4$ poises (from isochores)	Temperature 31.5° C. $\eta \times 10^4$ poises (from isochores)	Temperature 31.2° C. $\eta \times 10^4$ poises (from isochores)	Temperature 31.10° C. $\eta \times 10^4$ poises (from isochores)	Temperature 31.14° C. Density, gm. per cc.	Temperature 31.14° C. $\eta \times 10^4$ poises determined directly
0.548	4.040	4.040	4.040	4.040	0.502	3.791
0.527	3.835	3.850	3.870	3.890	0.489	3.744
0.502	3.640	3.700	3.770	3.810	0.475	3.694
0.480	3.465	3.555	3.680	3.755	0.462	3.652
0.471	3.370	3.450	3.590	3.700	0.442	3.293
0.464	3.295	3.375	3.500	3.625	0.422	3.100
0.457	3.235	3.310	3.425	3.535	0.397	2.845
0.452	3.200	3.255	3.365	3.445		
0.445	3.140	3.200	3.295	3.360		
0.437	3.065	3.100	3.185	3.260		
0.425	2.960	3.000	3.075	3.140		
0.410	2.850	2.880	2.970	3.025		
0.375	2.610	2.610	2.610	2.610		
0.356	2.490	2.490	2.490			

Time Lags

Quite early in this investigation it was noticed that a longer time was required for the viscosity to reach equilibrium when the temperature was raised from below the critical temperature to some temperature above, than when the system was cooled after it had come to equilibrium at some temperature above the critical. Once the system had reached equilibrium above the critical there was no time lag on heating further above the critical temperature. That is, the time lags occurred only when the system underwent the change occurring at the critical temperature. Geddes and Maass (9) found with ethylene that density equilibrium is reached faster on heating than on cooling, their measurements being made at constant pressure. They

interpreted their findings as evidence for a structure in the liquid state, which might be expected to require longer to form on cooling than to disperse on heating. It was believed that the time lags of viscosity at constant density were worth studying in some detail since they were in the opposite direction to those reported by Geddes and Maass.

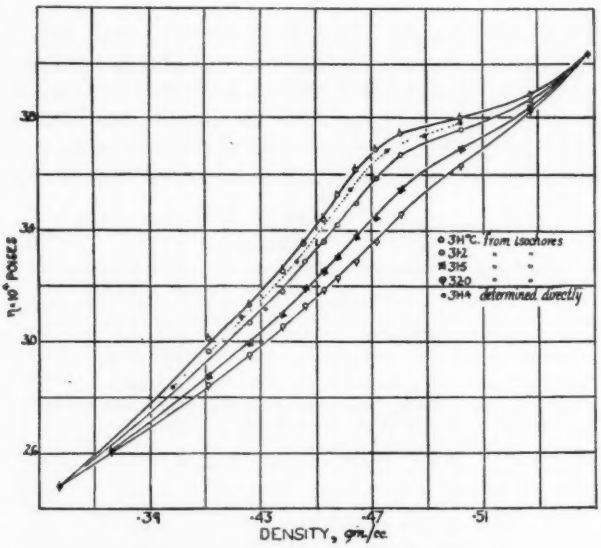

FIG. 2. *Isothermals of carbon dioxide.*

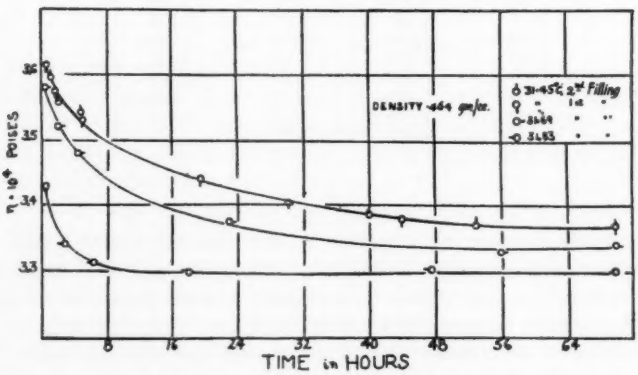

FIG. 3. *Time lags at the same density but different temperatures.*

On cooling the system down from above the critical temperature, there was no time lag beyond the time required for thermal equilibrium, which was about half an hour.

The time lags on heating the system were examined as follows: the bath was left at room temperature (22 to 24° C.) for several hours and then heated rapidly (at the rate of about two degrees in five minutes) up to the temperature at which time lags were to be measured, and the thermoregulator was set. Observations of viscosity were begun as soon as the system had reached thermal equilibrium and continued for long periods up to five days. Time was measured from that at which the thermostat reached the desired temperature to the midpoint of the observations at each time for which an observation of viscosity was made. An observation required about 20 to 30 min.

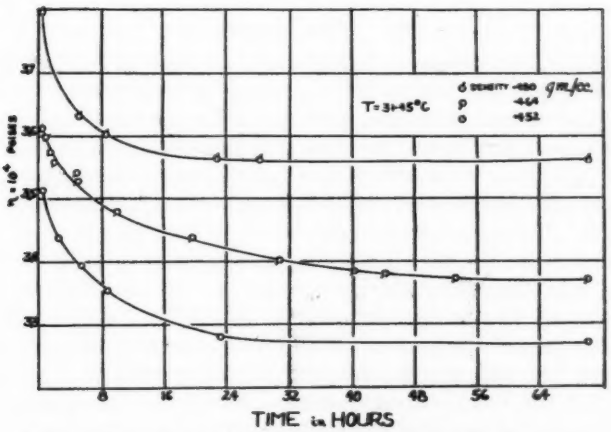

FIG. 4. *Time lags at different densities but at the same temperature.*

The data thus obtained are shown in Figs. 3 and 4. In all cases the final viscosity reached was the same as that found at the same temperature on cooling the system from several degrees above the critical. The end-point on each curve in Fig. 3 and 4 was obtained from the isochores of Fig. 1. The times required for the viscosity to reach a value halfway between this final value and the first measurement at one-half hour's time were estimated from the curves and are tabulated in Table III.

TABLE III

TIME LAGS

Time lags at constant density—0.464 gm. per cc.		*Time lags at constant temperature—31.45° C.*	
Temp., °C.	Time to half-value, hr.	Density, gm. per cc.	Time to half-value, hr.
31.45	9	0.480	2
31.69	6.5	0.464	9
31.83	2	0.452	5.5

All the curves in Fig. 3 are for time lags at the same density but at different temperatures. From these curves and the times to half value given in Table III, it will be observed that the time lags decrease regularly as the temperature is raised further above the critical. At 31.45° C. the time lag measurements were repeated with a different sample of carbon dioxide, and are plotted differently in the figure. The time lags of the two samples are similar, showing that the effect is probably not due to an impurity.

In Fig. 4, time lags are plotted for different densities at the same temperature, with times to half-value given in Table III. The time lags are greater nearer the critical density.

Discussion

The form of the viscosity-temperature isochores is not the same as that found by Mason and Maass (12) for ethylene, in that there is no minimum at the classical critical temperature, 31.1° C., nor even up to 7° C. above. For this region just above the critical temperature, the viscosity is seen to be more dependent on density than on temperature, the isochores being quite flat along the temperature axis, but the individual isochores being well separated. The isothermals, however, show that between an upper and a lower limit of density, the viscosity is also dependent to some extent on temperature, since the individual isothermals in the viscosity-density diagram are separated. This is contrary to the findings of Phillips (17) who found that the values of viscosity at all temperatures, if plotted against density, fell on one line; this would indicate that the viscosity is dependent only on density and not at all on temperature. With ethyl ether, however, Schröer and Becker (19) found that the isothermals in the viscosity-density diagram were separated above a lower density limit. For the highest density examined by them, the isothermals were still divergent. The results of the present investigation are in better agreement with those of Schröer, with the additional discovery of an upper limit of density, beyond which the isothermals are not separated.

Since the viscosity of a gas increases with rise in temperature, it can be predicted that ultimately the isochores in the viscosity-temperature diagram, Fig. 1, will show a minimum followed by a positive slope. For ethylene, Mason and Maass found the minimum viscosity at about 10.0° C. This laboratory has gathered considerable evidence (13, 14, 16) to indicate that liquid structure does not cease to exist at the classical critical temperature (9.5° C.) but persists up to 9.9° C. Therefore Mason and Maass interpreted their results as further evidence that liquid persists up to this temperature. The absence of a minimum in the viscosity-temperature isochores of carbon dioxide within 7° of the classical critical temperature might be interpreted as evidence that the liquid state persists beyond this temperature. Bradley, Browne, and Hale (2, 3, 4) found that adiabatic compression and expansion, caused by transferring the vibrations of a steel rod to the mercury surface in contact with the carbon dioxide in a Cailletet liquefaction apparatus,

gave rise to rippling and cloud formation at 8° C. above the critical temperature. They claimed that these results show strong evidence of the presence of liquid particles in the system at this temperature. On the other hand, precise measurements of the *P-V-T* relations of carbon dioxide led Michels, Blaisse, and Michels (15) to conclude that if a region exists in which liquid persists above the critical temperature, it must be small.

The reason for the long time lags on heating the system at constant density is not obvious. These findings do not constitute a direct contradiction of the findings of Geddes and Maass (9), who found a greater time lag on cooling the ethylene system than on heating it, since their observations were made at constant pressure whereas the present observations were made at constant density. Moreover, they used density as the criterion of equilibrium; viscosity was used in the present investigation. Geddes and Maass suggested that the time lags that they observed are due to a structure in the liquid state, which might be expected to take longer to form on cooling than to disperse on heating. The time lags in the opposite direction found by the present investigators would appear to detract from the exactness of this hypothesis. Since the two sets of observations were made on different systems, under different conditions, and using different criteria of equilibrium, it would appear to be unwise to attempt to explain the apparent conflict, until further observations have been made under more similar conditions.

At the present time no alternative explanation is apparent for the time lags observed by Geddes and Maass. To explain the time lags in the opposite direction found in the present investigation, it is suggested that a dispersion of liquid and vapour forms when the temperature is raised above the condensation temperature or "critical dispersion temperature" (16). Evidence that this occurs in the ethane system (13) and in the ethylene system (16) has already been published. This would require that the two phases come into contact and the necessary diffusion might be slow, resulting in long time lags such as have been observed. Failure to allow the system sufficient time to come to equilibrium would result in the appearance of hysteresis. Such hysteresis was observed by Clark (5, 6, 7). Moreover, Clark observed that stirring decreased the discontinuity. Harvey and Maass (10) have observed that the specific heat of carbon dioxide in the critical region is greater on heating from below the critical temperature than on cooling the system from well above this temperature. However, the specific heat on heating gradually drops to the value at the same temperature on cooling, if sufficient time is allowed. These phenomena are easily explained by the hypothesis that in the equilibrium state above the condensation temperature a dispersion of liquid and vapour is present. Of course, a corollary of this hypothesis is that the liquid state persists within some temperature interval above the classical critical temperature.

The present investigation confirms the conclusion that there is a fundamental difference between the liquid and gaseous states of aggregation. The form of the isochores, for example, indicates that the natures of liquid and gas are

different. Above the point of condensation the different isochores are well differentiated, and the viscosity appears to be more dependent on density than on temperature. At the condensation temperature, however, the isochores converge, and for the liquid phase the viscosity appears to be much less dependent on density, and considerably more dependent on temperature.

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